Measurements of phosphorus content in Lake Tahoe aerosols; past, present, and future

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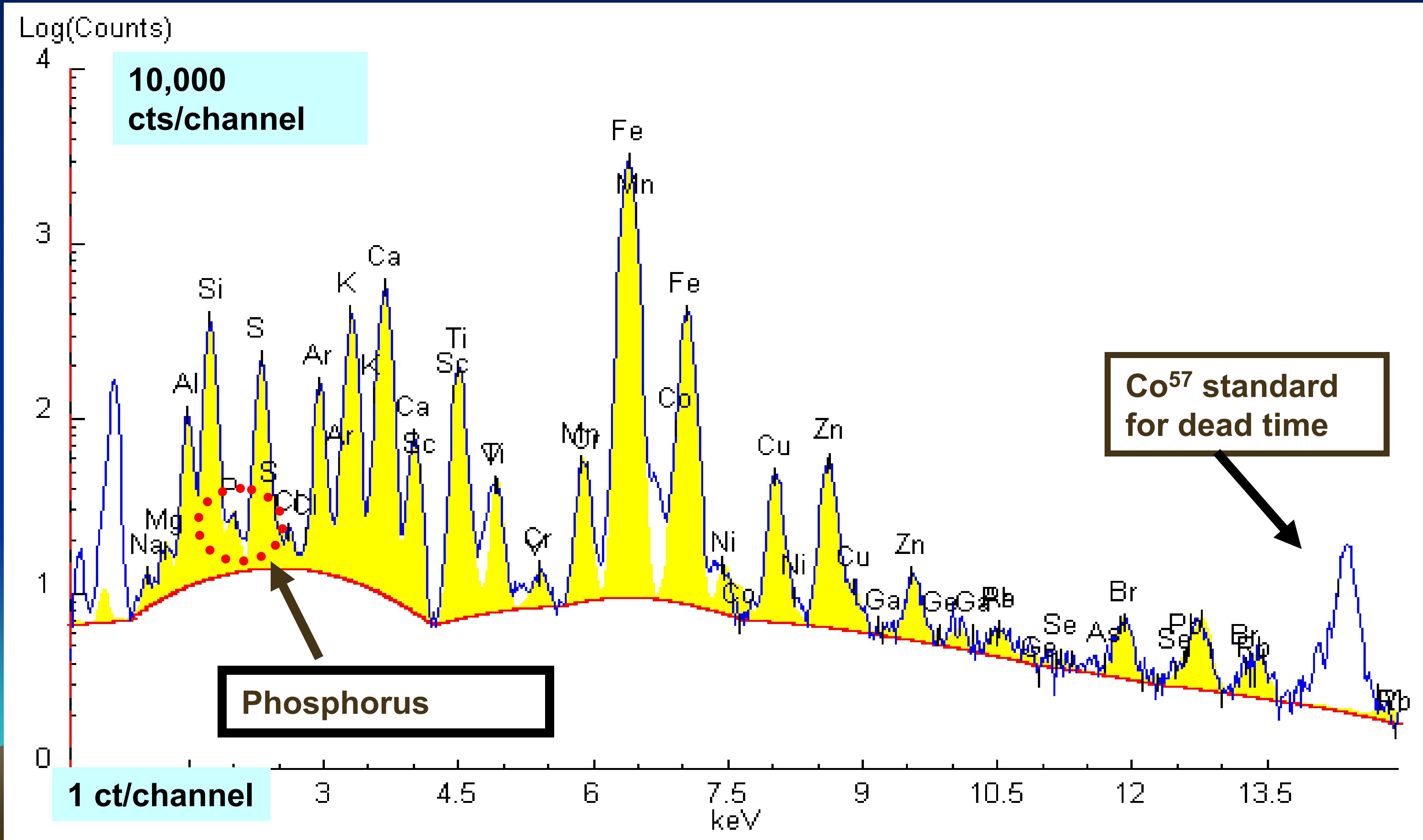
- Phosphorus is an important nutrient limiting algal growth.
- Tahoe Research Group (TERC) deposition buckets on the lake show significant dry deposition of phosphorus between 6 tonnes and 9 tonnes/year, roughly 20% of all phosphorus input.
- However, measurements of phosphorus in atmospheric aerosols from ARB (1977-1979) and TRPA (1988-present) studies show very little airborne phosphorus.
- In this summary, I will
  - Examine the sources of the problem and why phosphorus was rarely seen in the past,
  - give my analysis of two recent studies, TRPA and LTAD, and
  - propose methods to measure phosphorus aerosols at Lake Tahoe for future work.

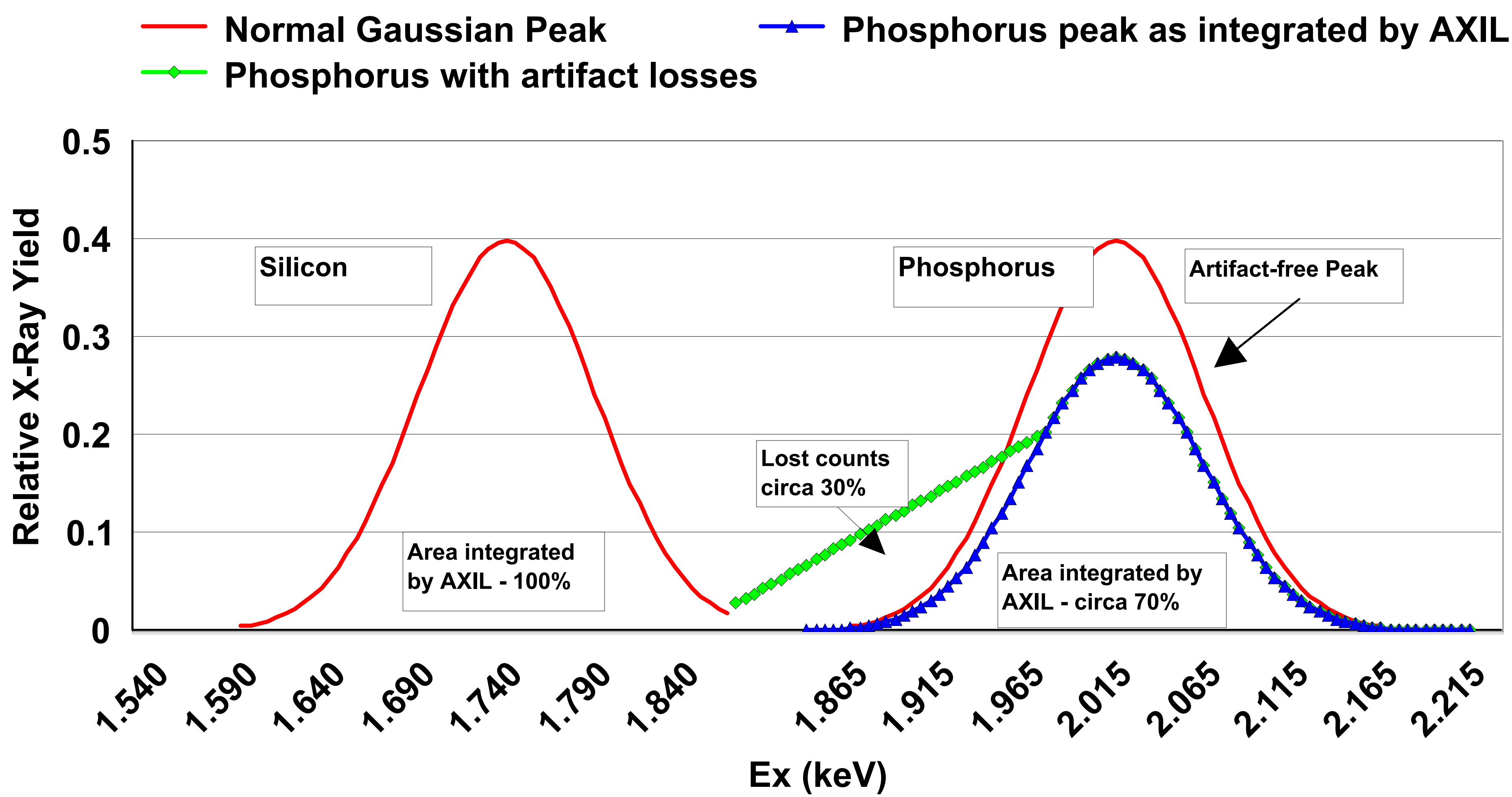
Why is phosphorus so hard to measure at Lake Tahoe? – Problems!

- General: Aerosol levels at Lake Tahoe are low, so many standard sampling/analytical methods are ineffective.
- P #1: Phosphorus is a geochemically rare element, at levels roughly 0.5% of silicon in igneous rocks,
- In x-ray analysis used in past ARB, DRI, and TRPA studies,
  - P #2: Phosphorus falls close to a massive silicon peak and it needs excellent detectors and software to spectrally resolve,
  - P #3: Phosphorus x-rays self-absorb in the standard Si(Li) detectors, losing roughly 30 % of all x-rays to heat,
  - P #4: Phosphorus in an alumino-silica matrix is highly absorbed by both the Al and Si, roughly a factor of 3 versus Si.
- There are no NIST or commercial stochiometric secondary phosphorus aerosol standards.

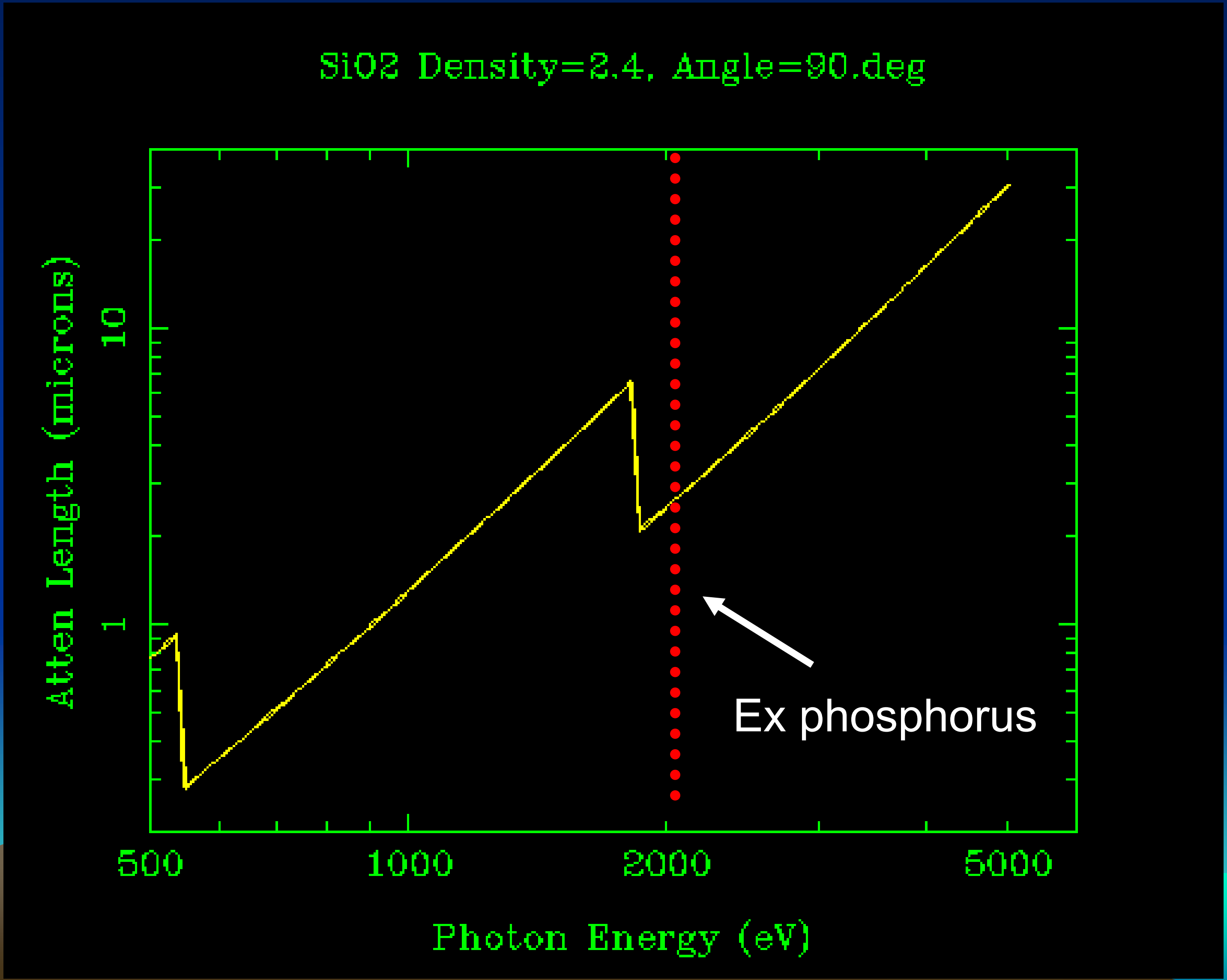
Problem #1,Problem #2: Synchrotron-X-Ray Fluorescence (S-XRF) spectrum and AXIL analysis of an LTAD raft aerosol sample. The S-XRF beam helps by suppressing the Si peak by a factor of about 4 and background by a factor of 100.



Problem # 3: Phosphorus loss in Si(Li) x-ray detectors – needs a times 1.42 correction



Problem #4: Enhanced (x 3) self absorption of phosphorus x-rays in an alumino-silica (soil) matrix



Summary of problems with phosphorus

- Low aerosol mass values at Lake Tahoe - not much mass to analyze
- Phosphorus is only 0.5% of silicon in igneous rock
- Much of the phosphorus at Lake Tahoe occurs in particles > 2.5 µm
  - Thus not seen on earlier $PM_{2.5}$ filters
  - PM_{10} filters not analyzed by TRPA/IMPROVE
  - Significant phosphorus above 10 µm not even sampled
- Phosphorus loss in detectors – 30%
  - Corrected only by IMPROVE
- Phosphorus enhanced self absorption in soil – 68%
  - All groups ignored this problem

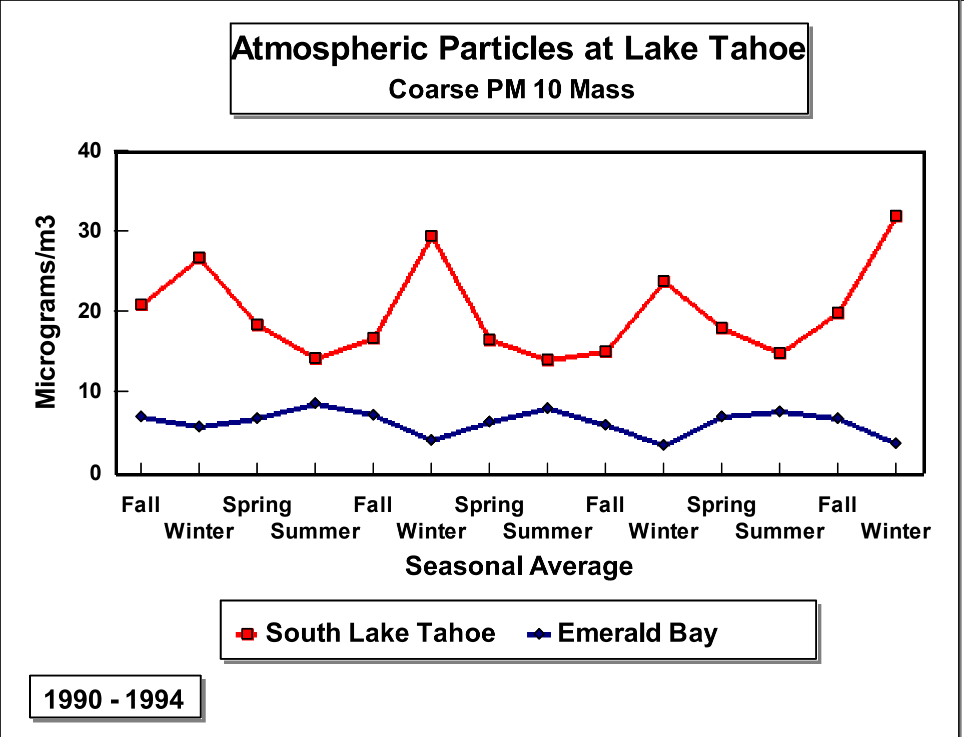
Thus the detection of phosphorus in a 9 µm soil particle is ~ 1000 times harder than detection of silicon

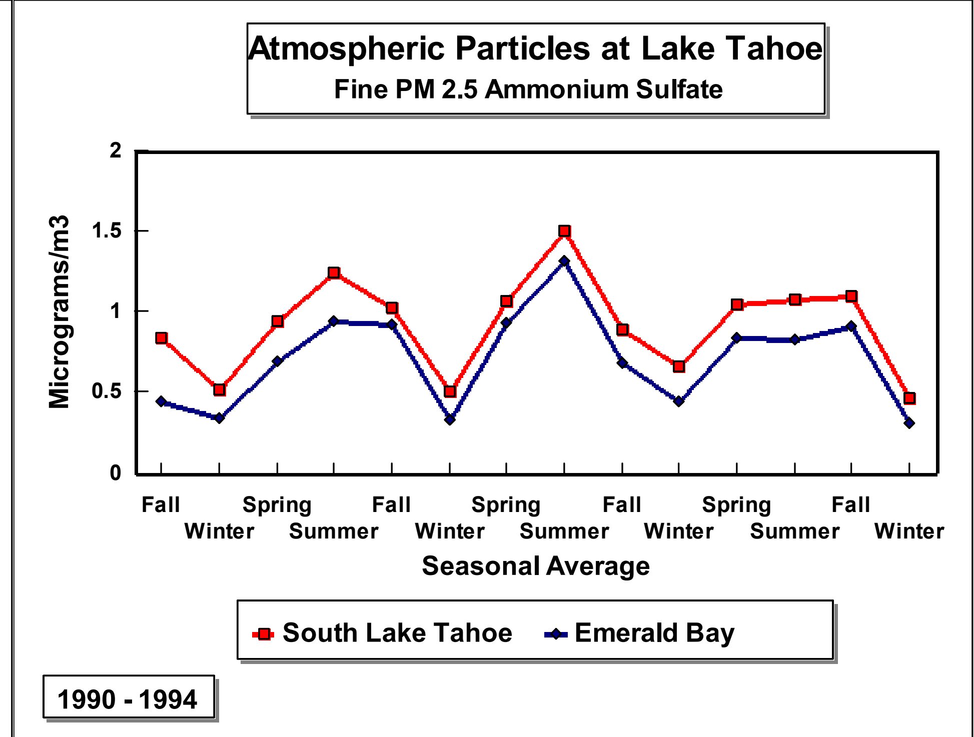
Analysis of phosphorus in past studies

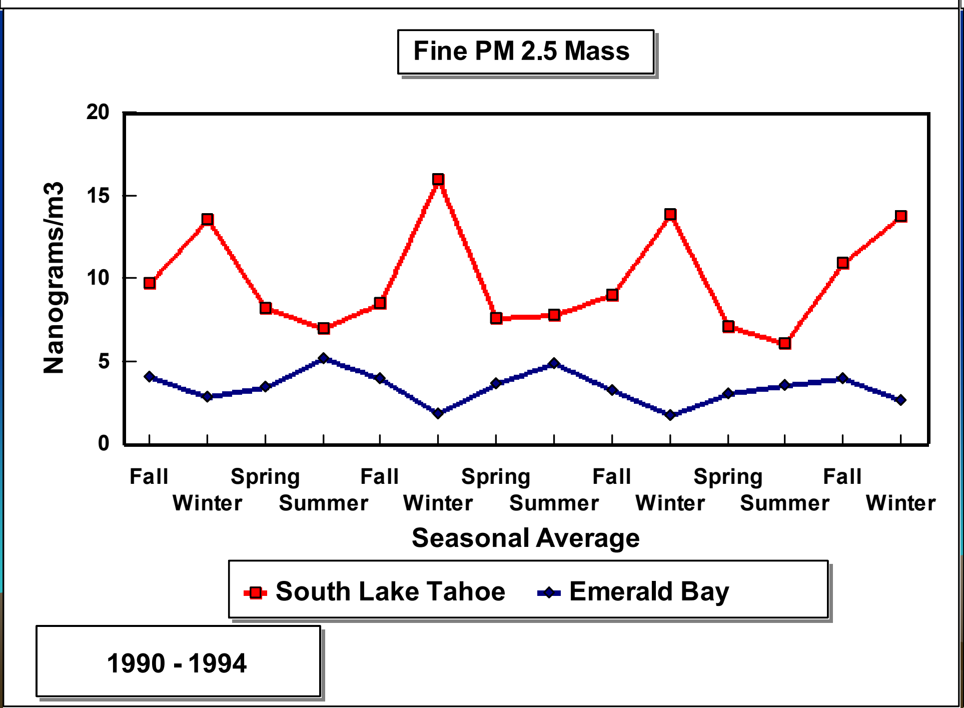
- UCD/ARB 1977-1979 - 9 sites, Sierra crest and basin
  - Wide spatial and temporal (6 mo.) coverage; archived filters
  - Weak analytical methods; No reason to push for phosphorus
- UCD/ARS/TRPA Bliss and SOLA, 1988 - 2001
  - Only $PM_{2.5}$ filters analyzed (PM_{10} collected, archived)
  - Moderate sensitivity - some phosphorus data
- IMPROVE Bliss SP 2001 – present
  - Weak analytical methods for $PM_{2.5}$ filters – no phosphorus data
  - No longer able to analyze PM_{10} filters
- UCD/TRPA/ SOLA 2003
  - Single highly impacted site (now adding ARB Sandy Way site)
  - Non Federal Reference sampling – DRUM impactor
  - Excellent size (8 size cuts to 35 μm) and time (3 hr) resolution
  - S-XRF high sensitivity – 5,400 phosphorus values
  - LTAM USFS model – extrapolate and predict deposition

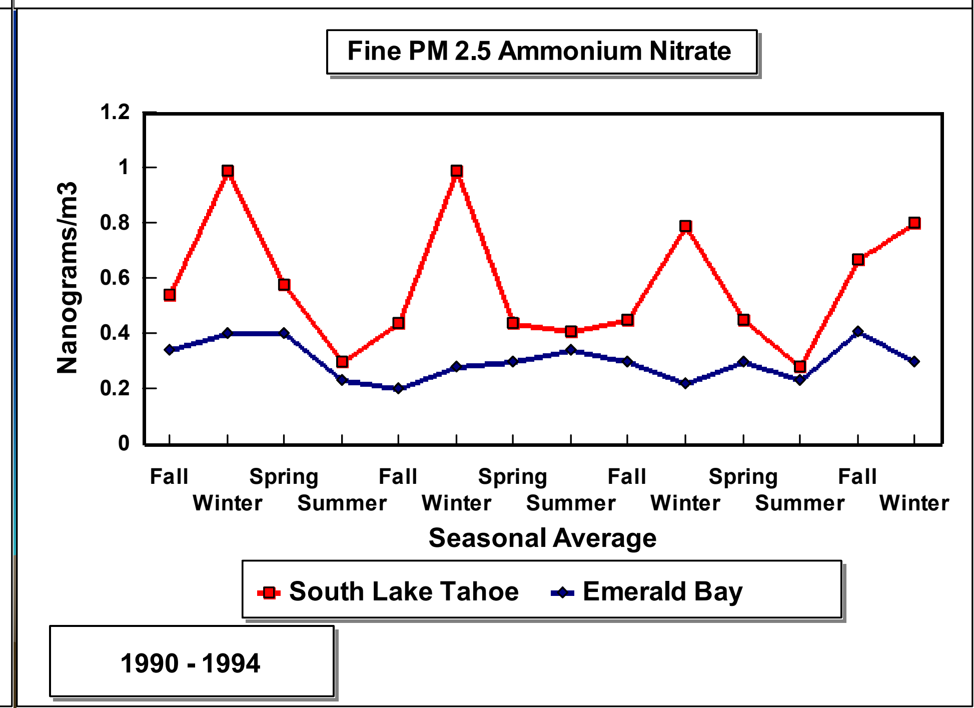
TRPA- Air Resource Specialists/UC Davis visibility sampling – aerosols- Bliss and South Lake Tahoe (SOLA) 1988 - present

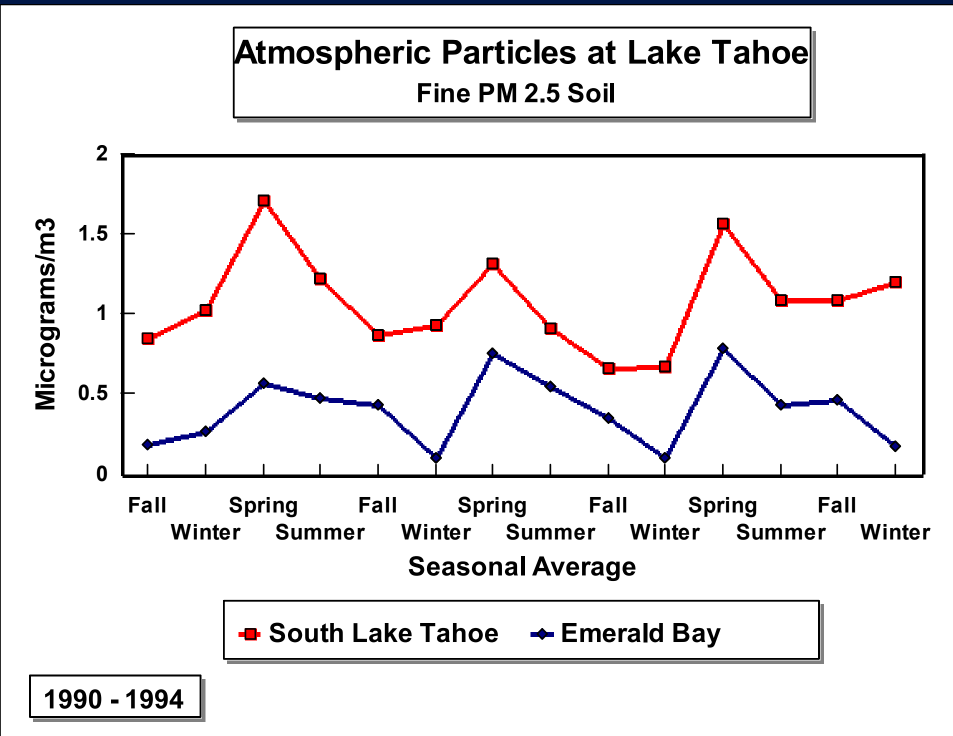
- Sampling sites based on prior ARB /UCD studies
  - Bliss Sate Park (250 m above the lake) = Sierra Ski Ranch and Desolation Wilderness
- Wednesday – Saturday 24 hr average
- IMPROVE protocols
  - redundant mass and mass closure
  - Redundant organics (8 temp categories DRI + PESA)
  - Ions sulfates, nitrates (scrubbed)
  - Elements Na – Zr, some heavies

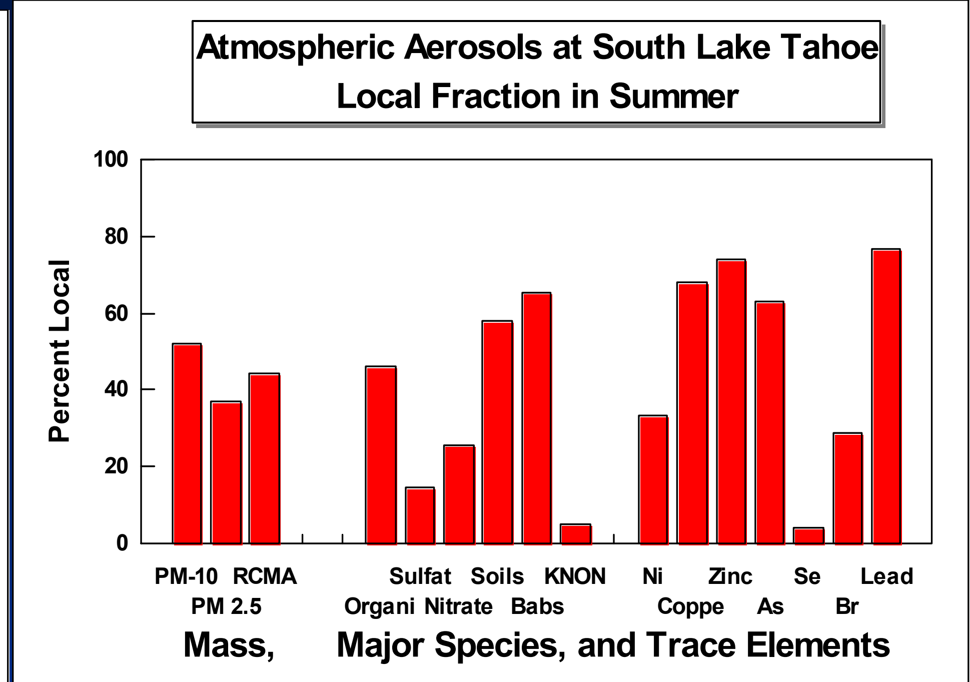

Atmospheric Particles at Lake Tahoe
Coarse PM 10 Mass
Micrograms/m3
0
10
20
30
40
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Seasonal Average
South Lake Tahoe
Emerald Bay
1990 - 1994

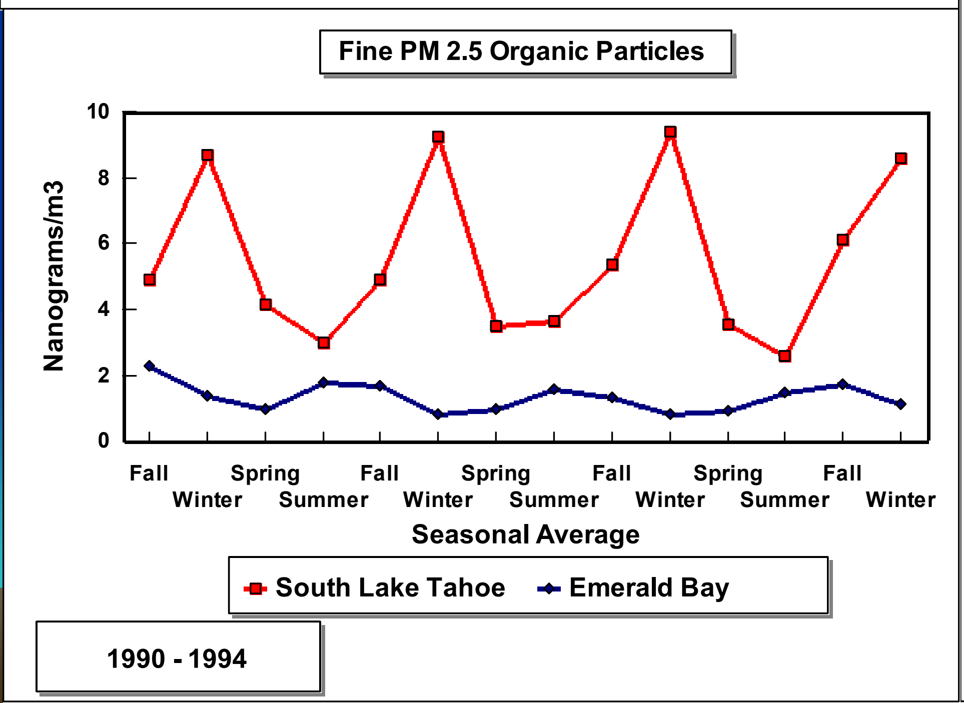

Atmospheric Particles at Lake Tahoe
Fine PM 2.5 Ammonium Sulfate
Micrograms/m3
0
0.5
1
1.5
2
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Seasonal Average
South Lake Tahoe
Emerald Bay
1990 - 1994

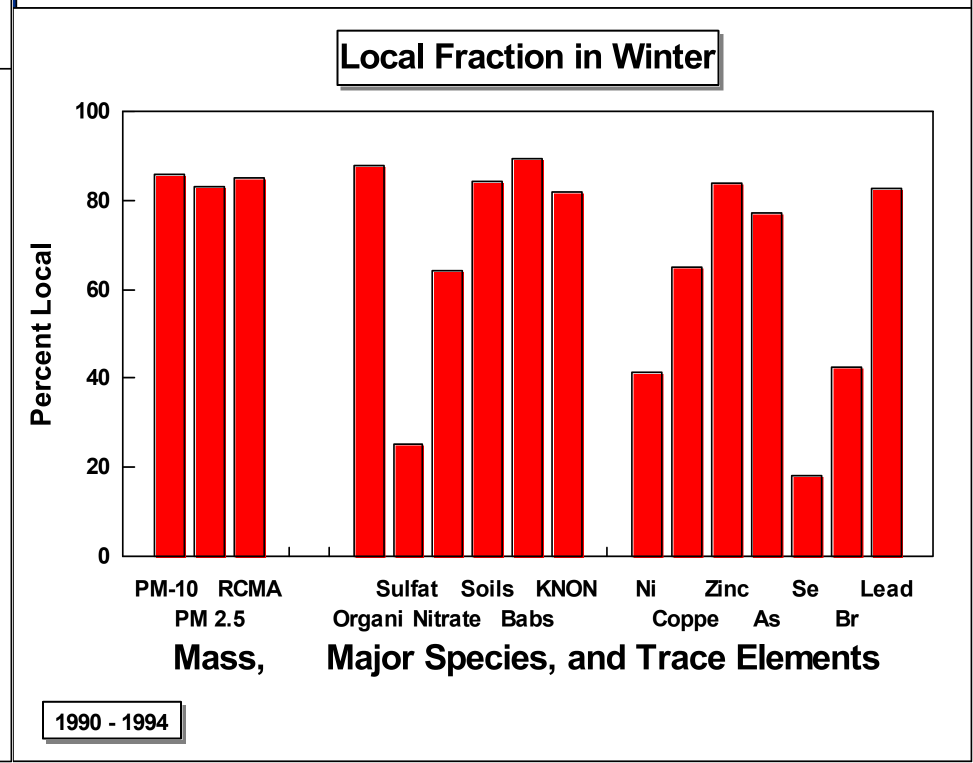

Fine PM 2.5 Mass
Nanograms/m3
0
5
10
15
20
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Seasonal Average
South Lake Tahoe
Emerald Bay
1990 - 1994

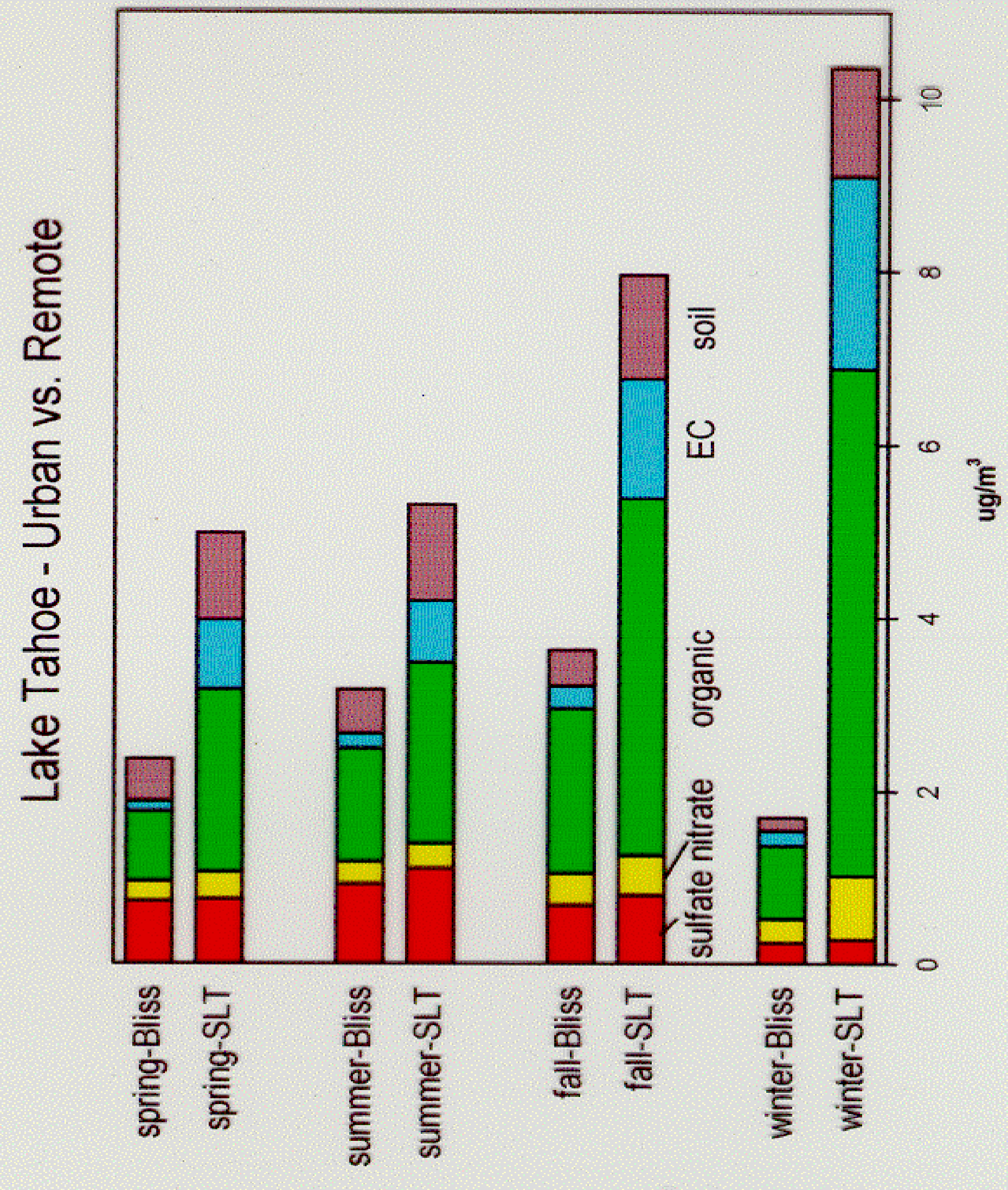

Fine PM 2.5 Ammonium Nitrate
Nanograms/m3
0
0.2
0.4
0.6
0.8
1
1.2
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Seasonal Average
South Lake Tahoe
Emerald Bay
1990 - 1994


Atmospheric Particles at Lake Tahoe
Fine PM 2.5 Soil
Micrograms/m3
2
1.5
1
0.5
0
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Seasonal Average
South Lake Tahoe
Emerald Bay
1990 - 1994


Atmospheric Aerosols at South Lake Tahoe
Local Fraction in Summer
Percent Local
100
80
60
40
20
0
PM-10
PM 2.5
RCMA
Organi
Sulfat
Nitrate
Soils
Babs
KNON
Ni
Coppe
Zinc
As
Se
Br
Lead
Mass,
Major Species, and Trace Elements


Fine PM 2.5 Organic Particles
Nanograms/m3
10
8
6
4
2
0
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Spring
Summer
Fall
Winter
Seasonal Average
South Lake Tahoe
Emerald Bay
1990 - 1994

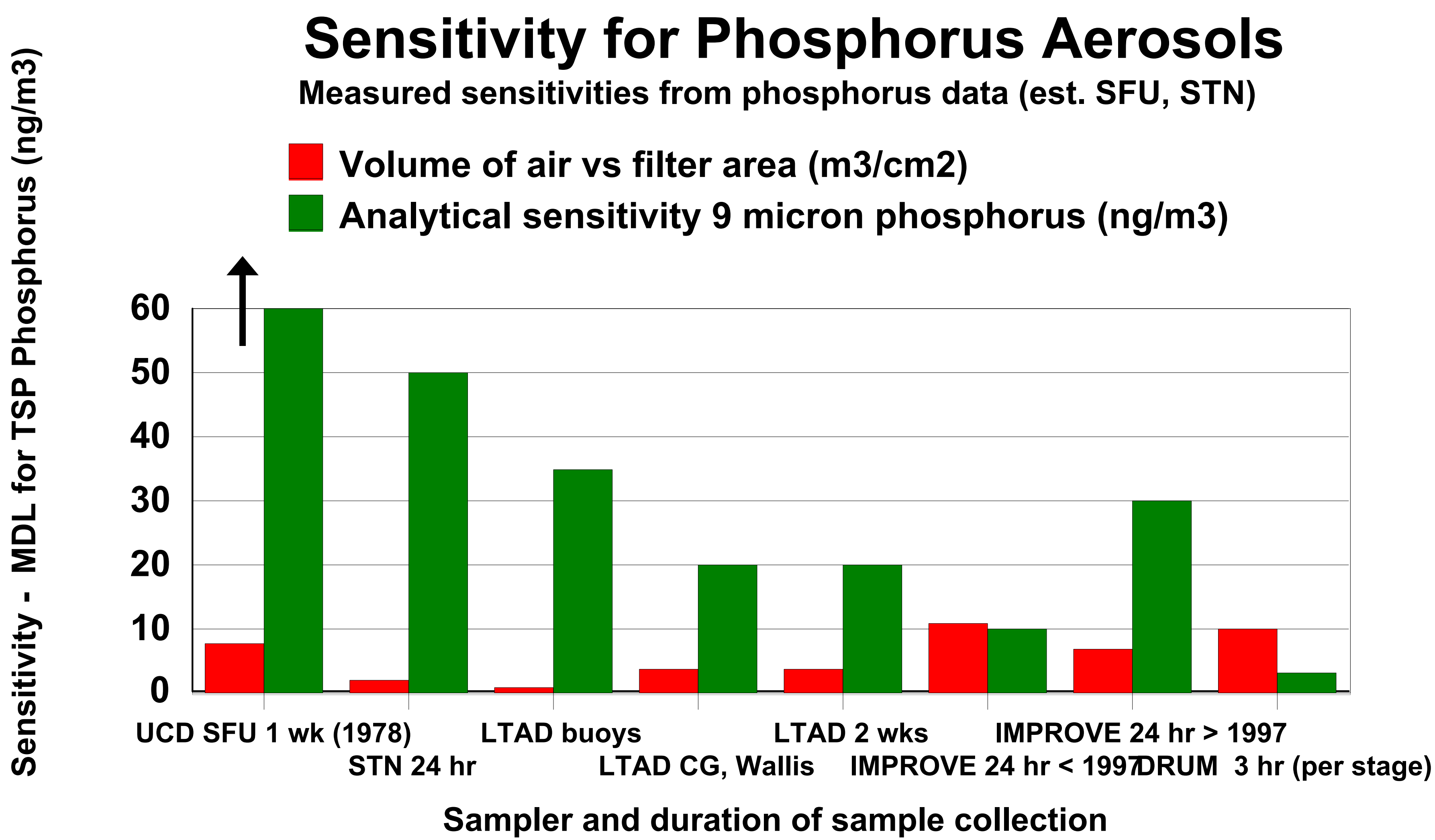

Local Fraction in Winter
Percent Local
100
80
60
40
20
0
PM-10
PM 2.5
RCMA
Organi
Sulfat
Nitrate
Soils
Babs
KNON
Ni
Coppe
Zinc
As
Se
Br
Lead
Mass,
Major Species, and Trace Elements
1990 - 1994



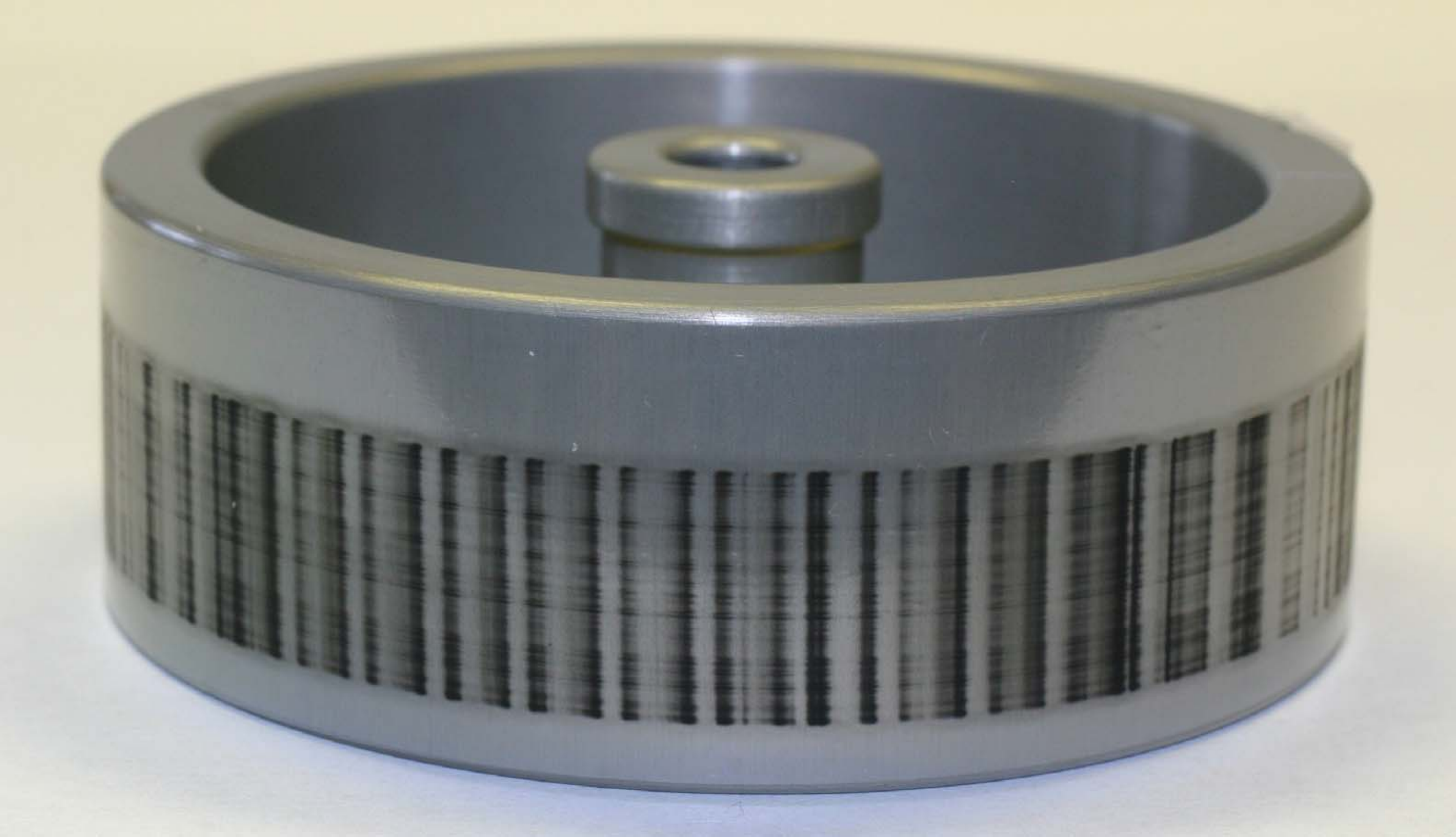
TRPA/ARS/UC Davis 3 year comparison Bliss SP versus SOLA

The areal density of the deposit (m^3/cm^2) is vital for XRF sensitivity when available mass is low -

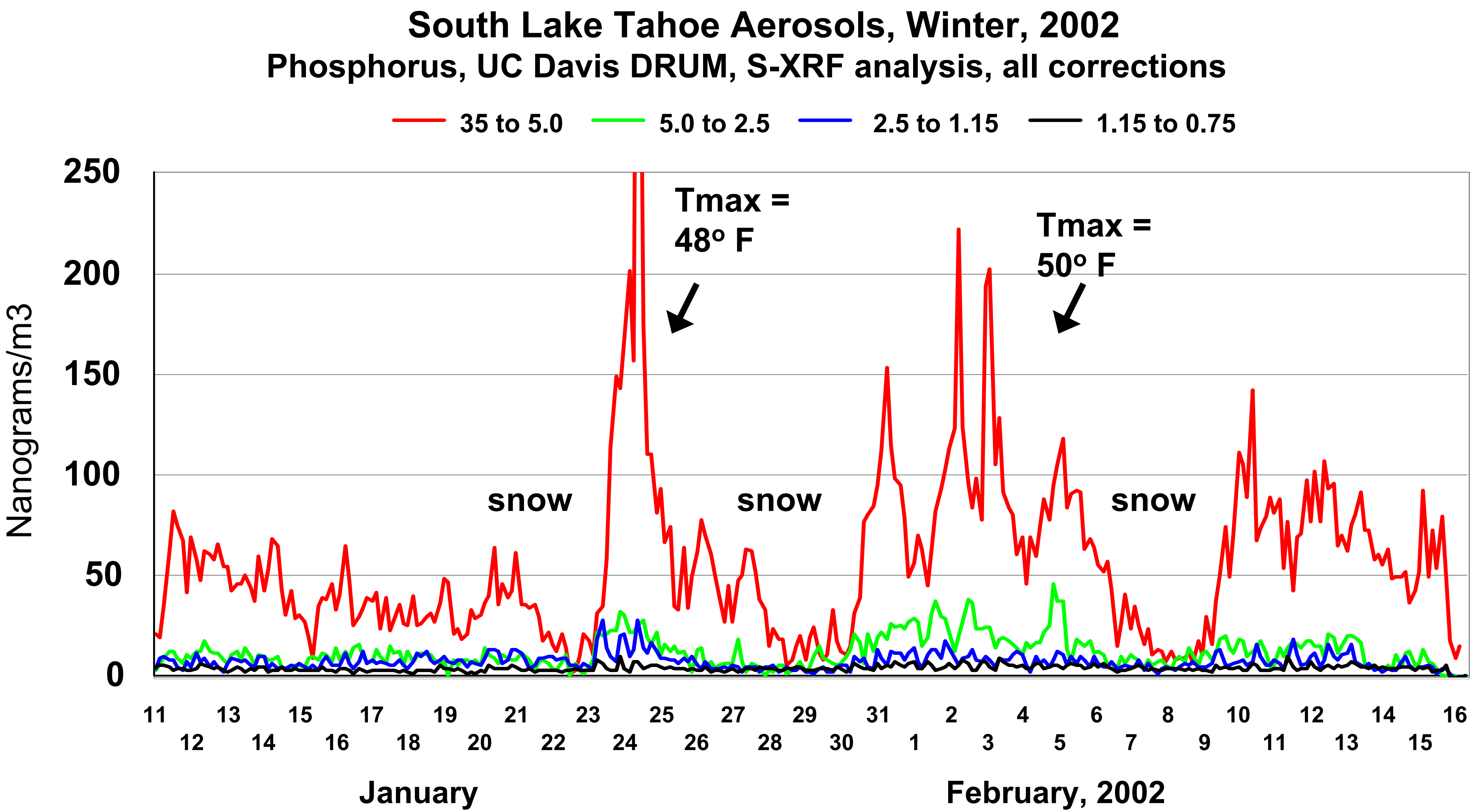
(Analysis MDL)ng/cm^2 x (Areal Density (ng/m^3) = (Aerosol MDL) ng/m^3



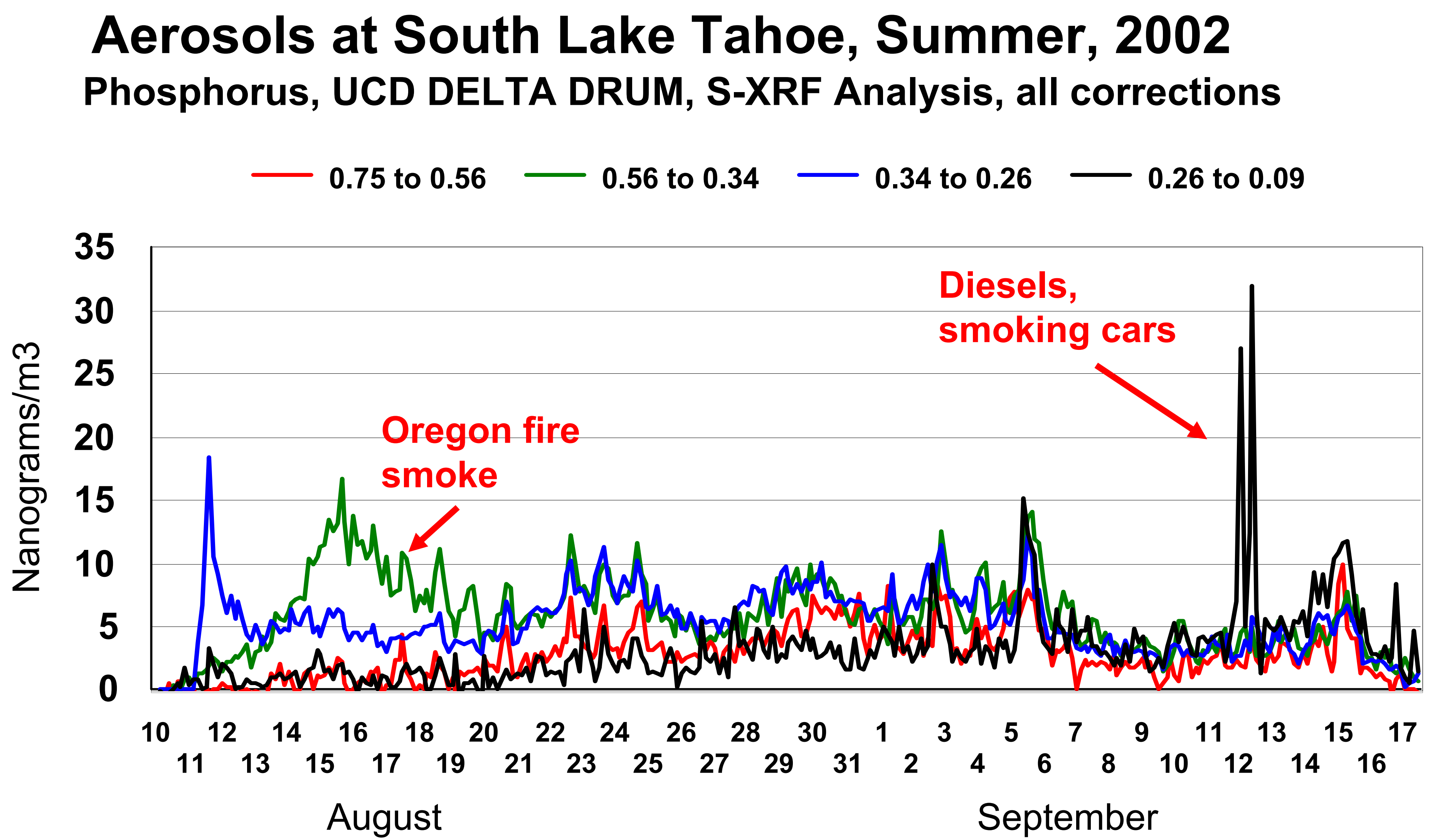
Example of 0.26 to 0.09 µm aerosols collected on a rotating drum impactor (DRUM) over 3 weeks at SOLA



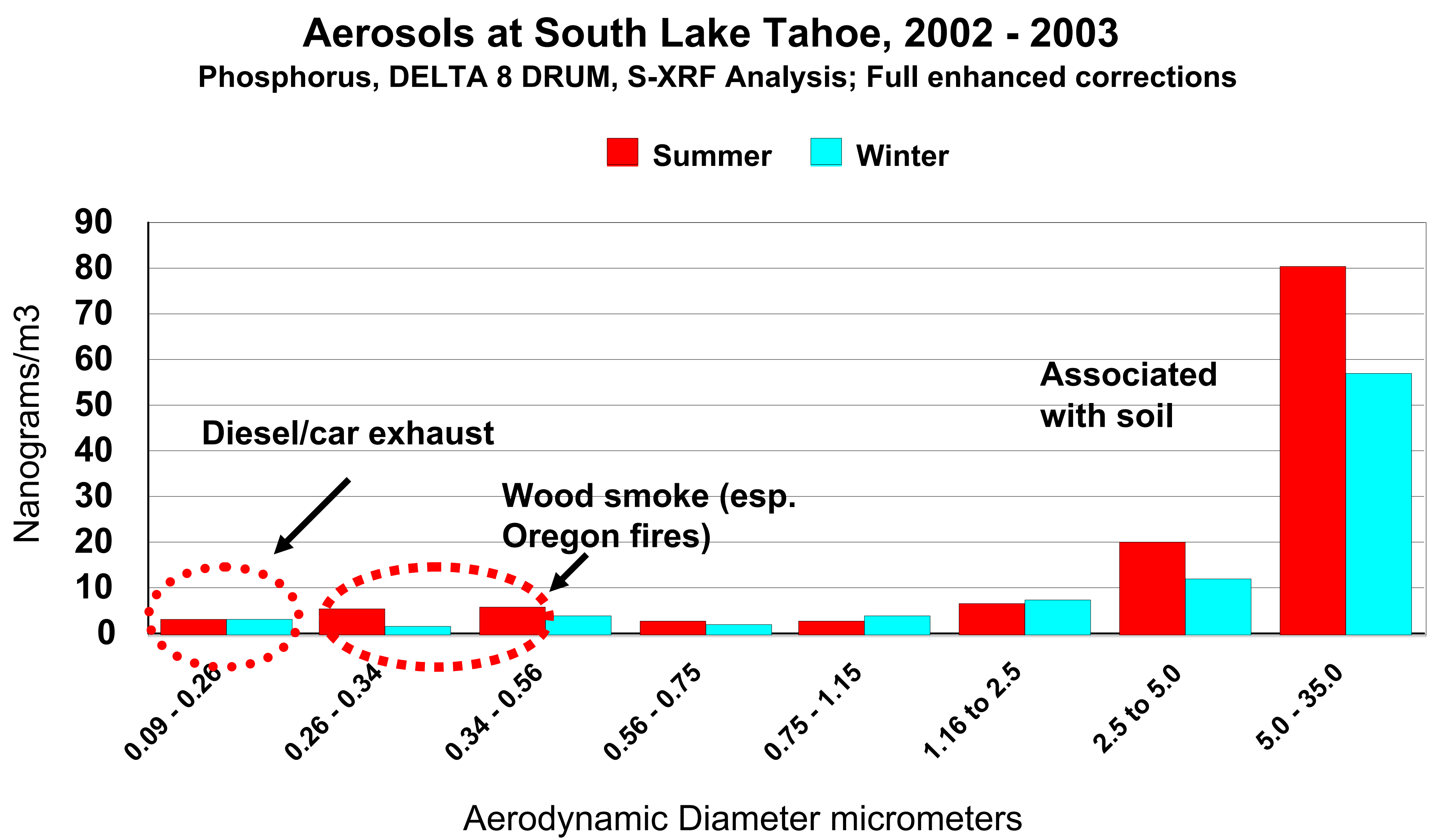
Winter phosphorus correlates with road sanding/salting activities



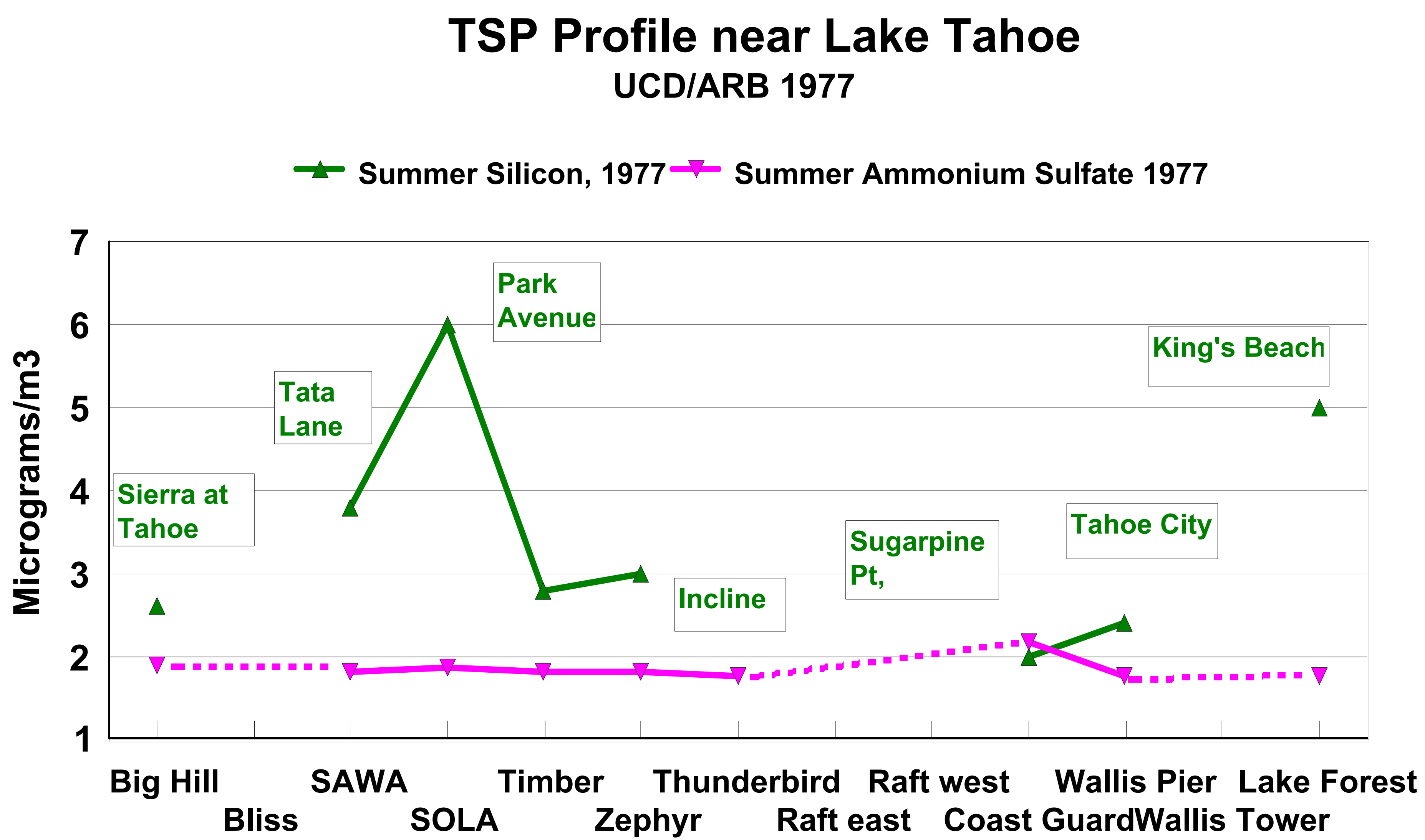
Phosphorus in summer from Wood Smoke and Diesels and Smoking Cars



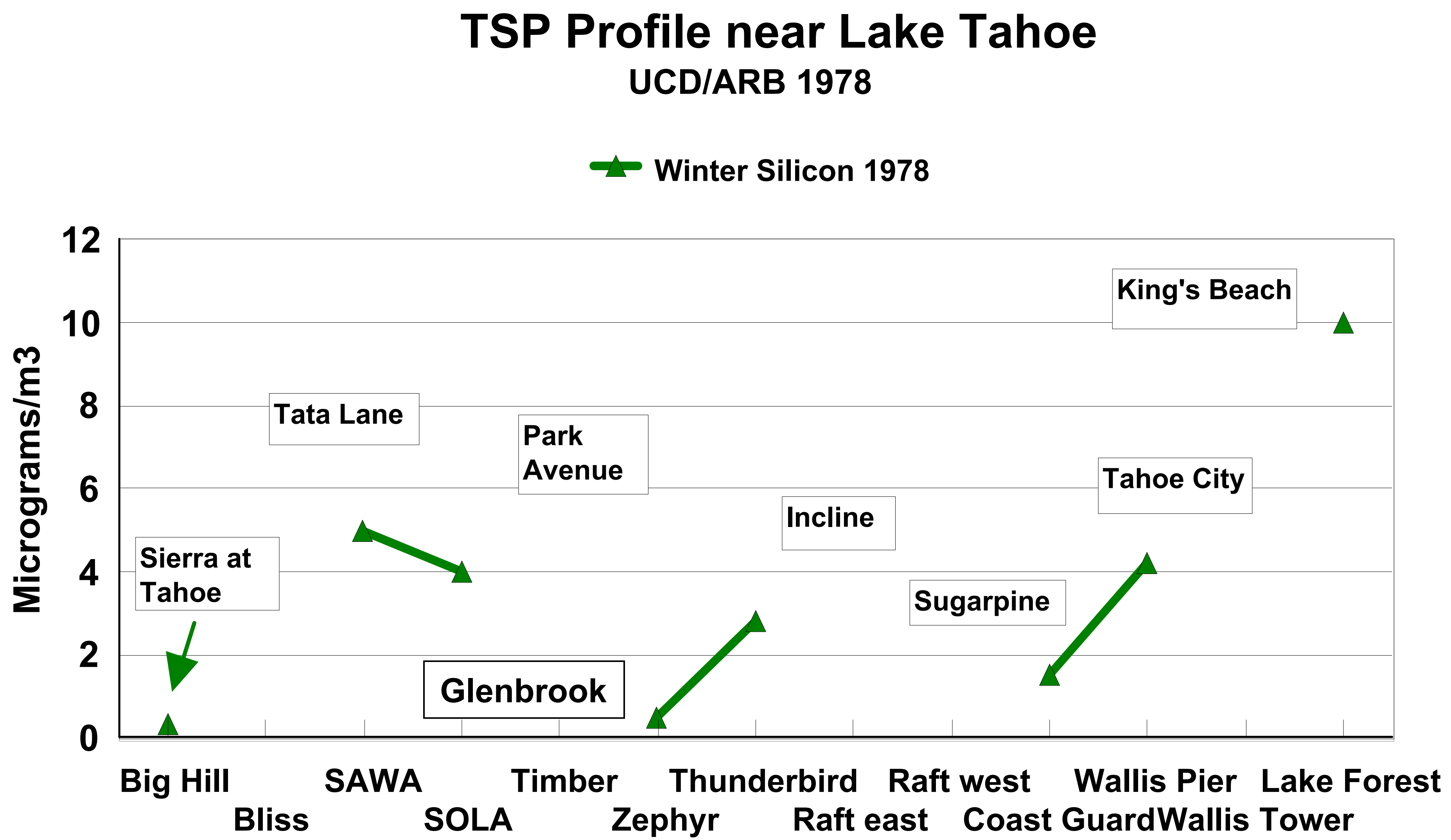
Phosphorus aerosols at South Lake Tahoe (SOLA) with all corrections



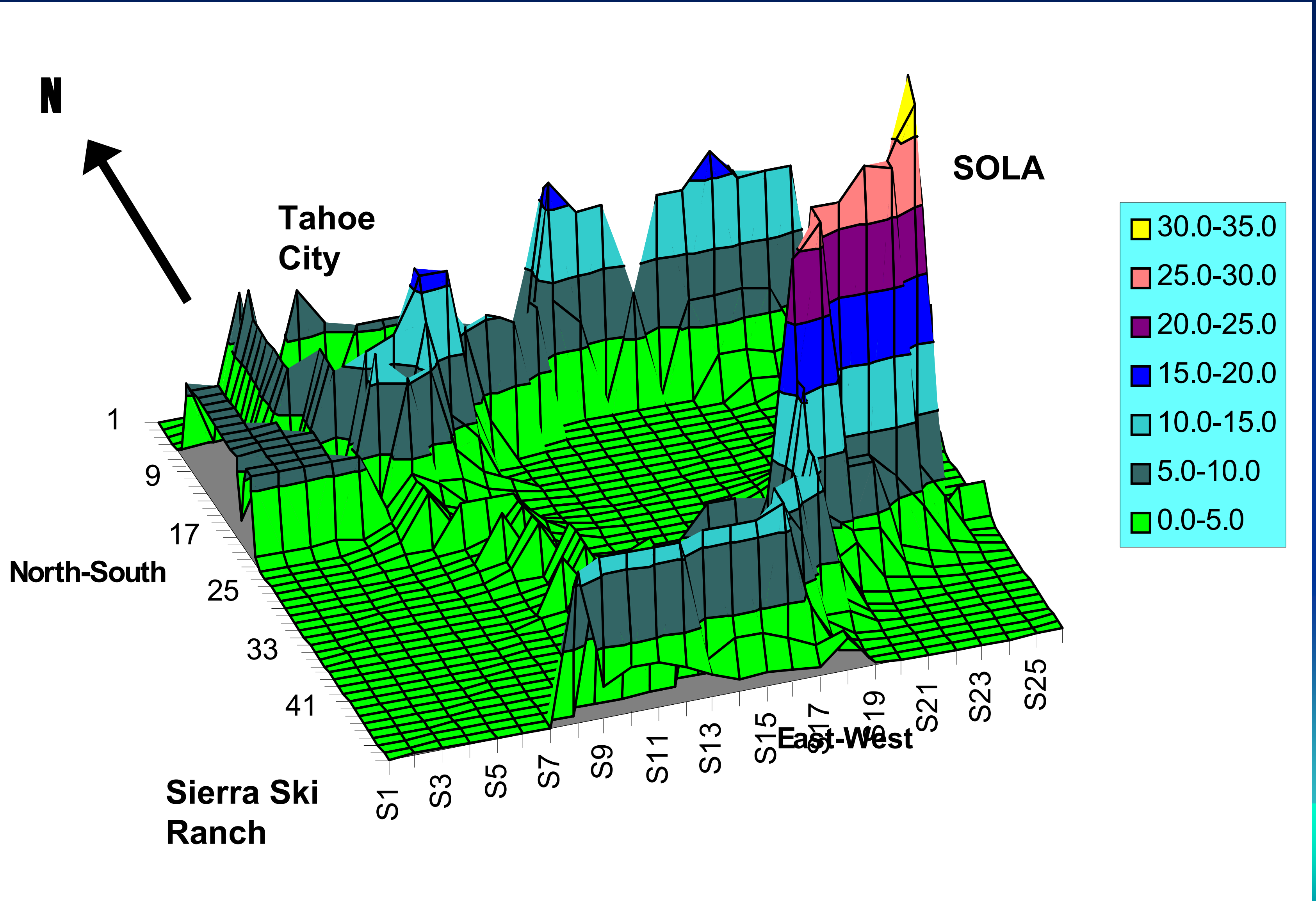
Data from the UCD/ARB 1977-1978 Contract A6-219-39 Summer



Data from the UCD/ARB 1977-1978 Contract A6-219-39 Winter



Winter phosphorus concentrations from coarse soil particles entered into the 1500 cell LTAM Eulerian Model (Cahill et al, 2000; Cahill 2004; needs corrections)



Results Of UCD/TRPA Analysis

(Cahill, 2004; Gertler et al, 2005 in press)

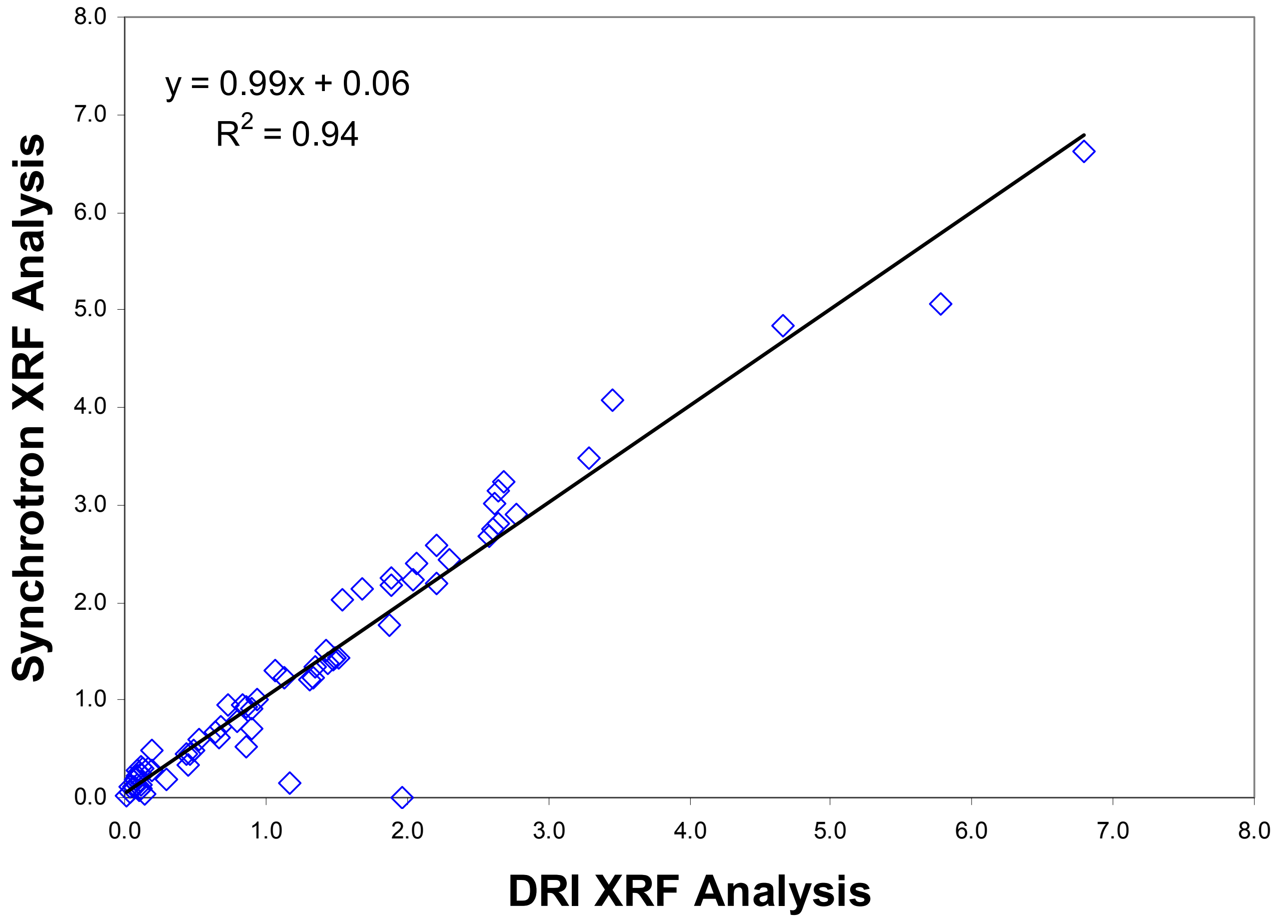
Source	Estimate (tonnes/yr)	Comments
• Asian dust	0.6 - 1.0	High phosphorus content
• Sac. Valley dust	0.12 - 0.6	Size unknown
• Smoke (Oregon, 2002)	0.2 - 0.3	Direct aerosol/deposition measured
• Highway soils - winter	3.5 – 5.0	New CalTrans size data - reduce
• Soils – spring to fall	1.5 – 4.5	Study in progress
• Vehicle exhaust	1.2 - 1.8	Need < 0.09 μm
• Local wood smoke	0.3 - 0.5	Highly variable in space/time
Total	7.4 – 8.5 - 13.7	

(See Gertler et al 2005, for explicit statements about the sources of the uncertainties in the estimates.)

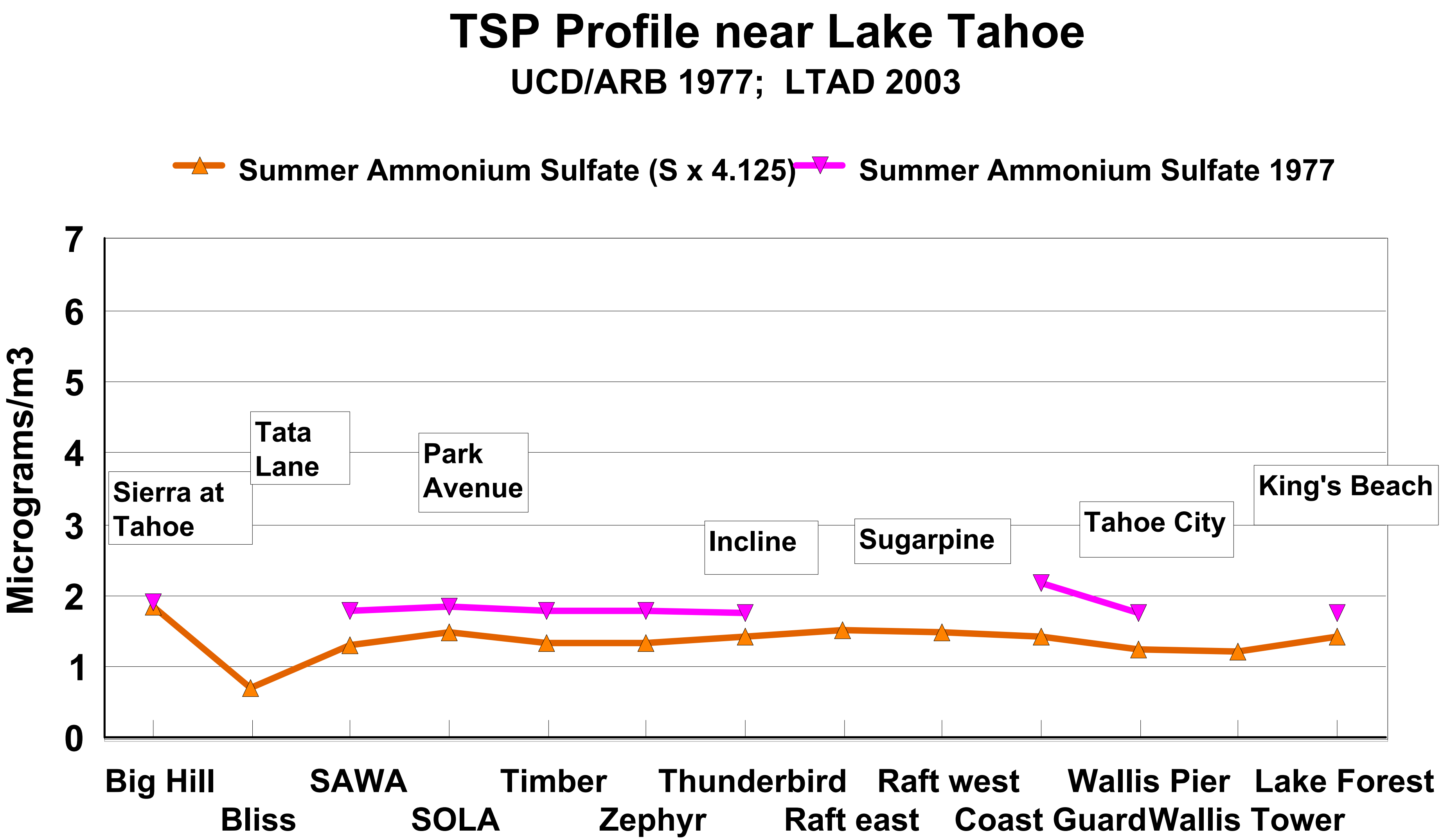
Future estimates will benefit from LTAD's 1. extensive meteorology, 2. Mid lake measurements, plus 3. better estimates of particle sizes, and 4. more direct phosphorus measurements.

Comparison of DRI XRF versus UCD DELTA Group S-XRF for major elements was uniformly excellent.

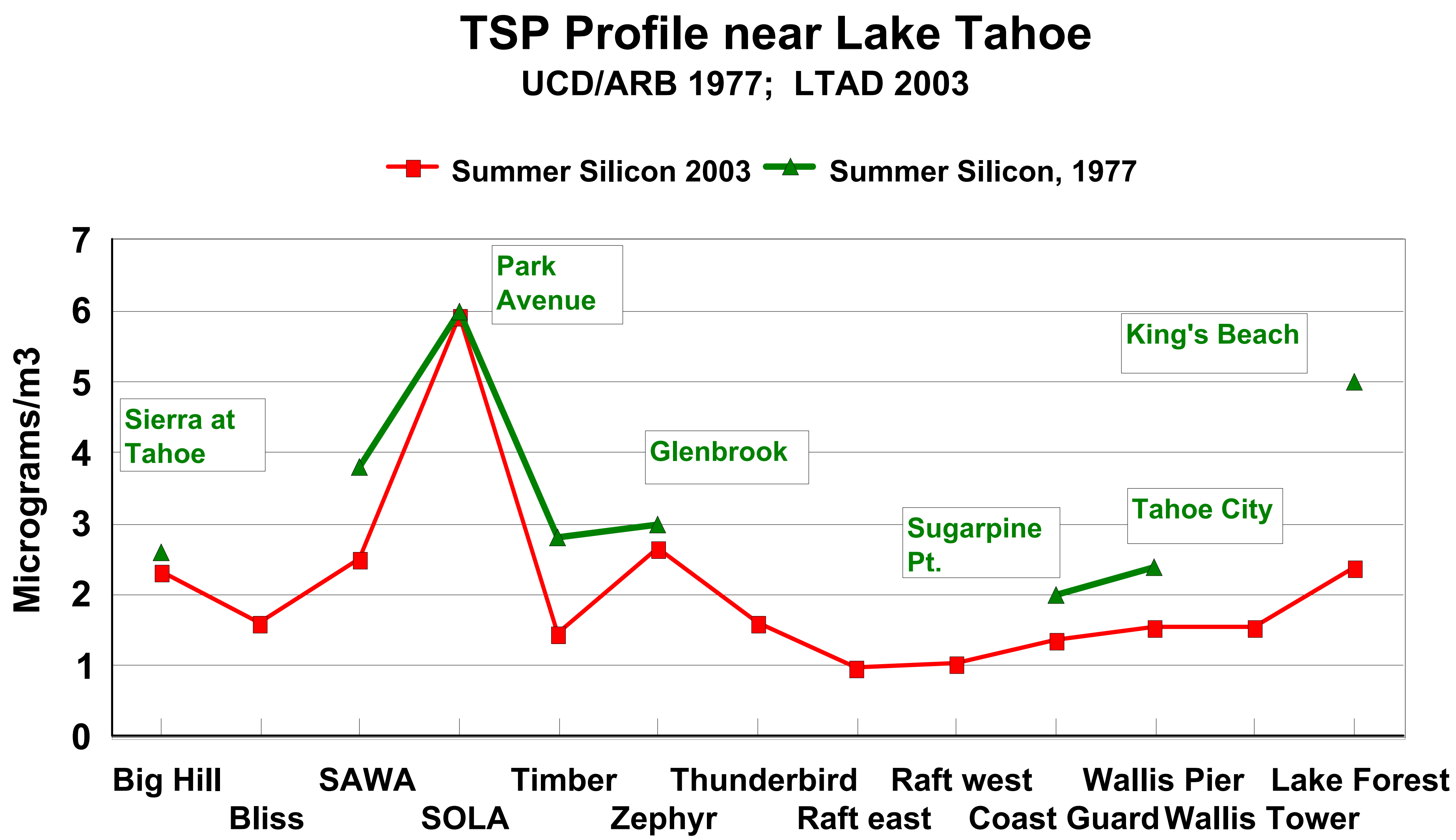
Silicon



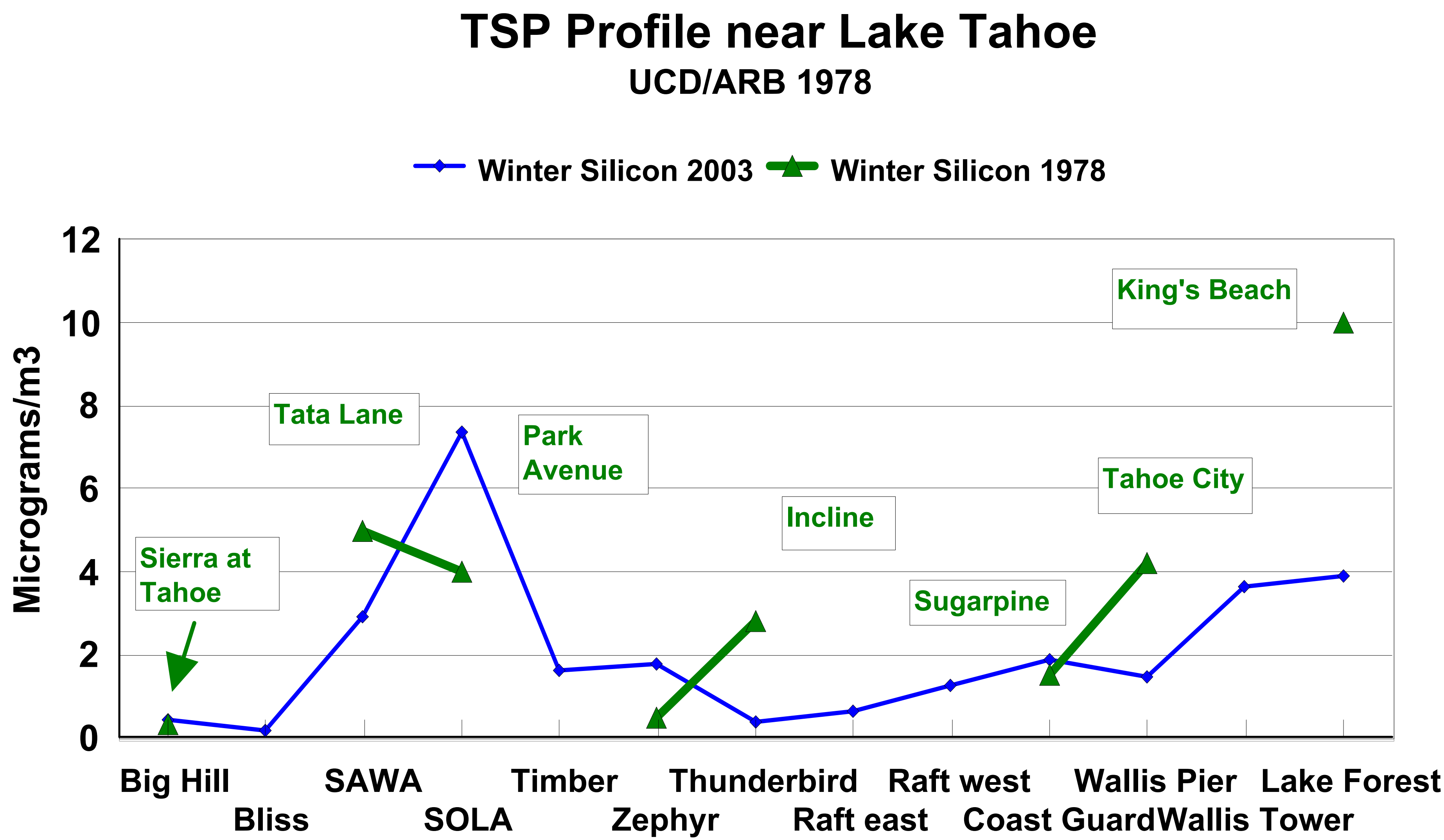
Data from LTAD 2005 and the UCD/ARB 1977-1978 Contract A6-219-39, Summer



Data from LTAD 2005 and the UCD/ARB 1977-1978 Contract A6-219-39, Summer



Data from LTAD 2005 and the UCD/ARB 1977-1978 Contract A6-219-39, Winter



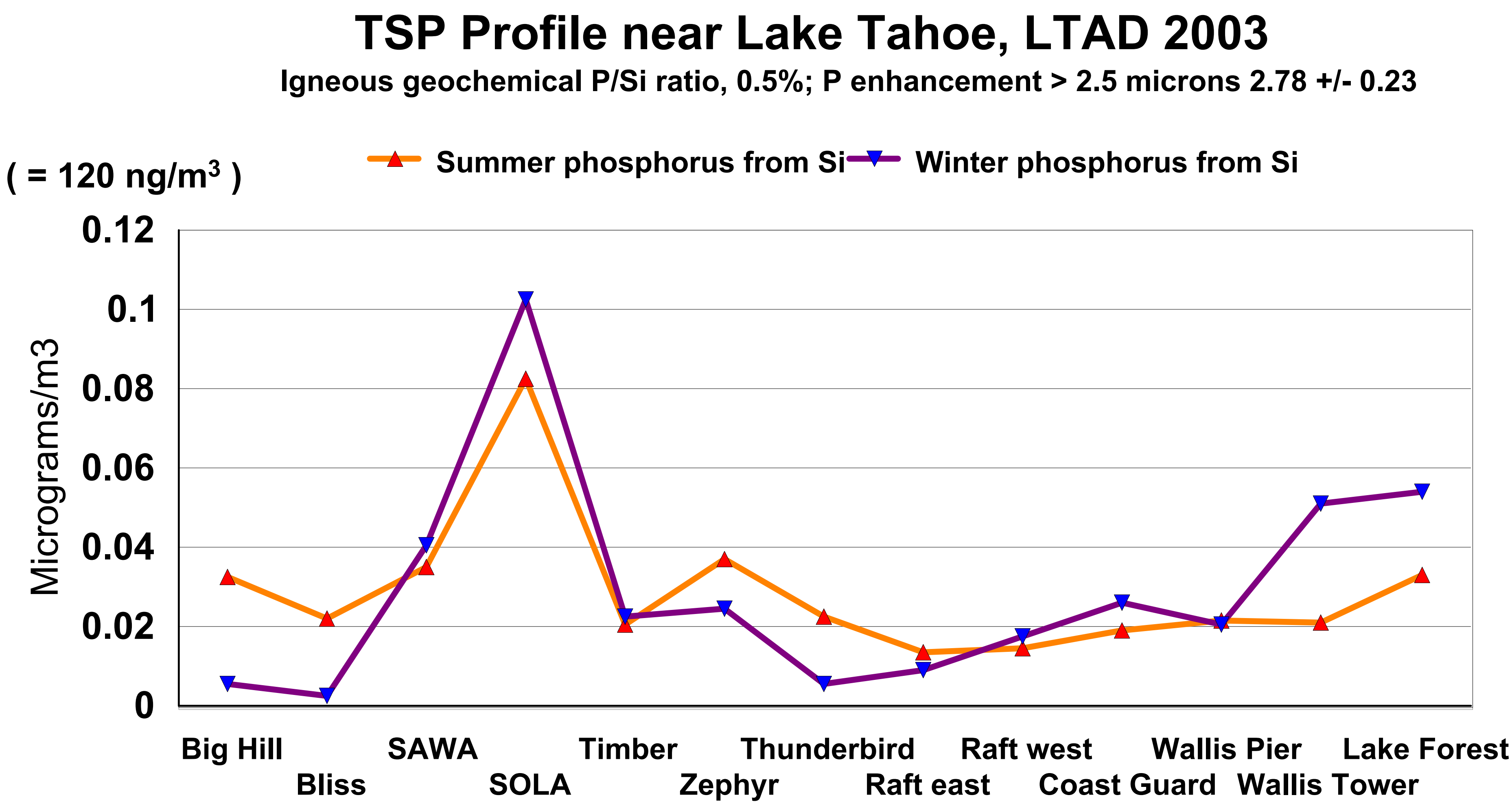
Phosphorus Measurements in LTAD

- Circa 540 aerosol samples were collected at many sites for over a year, including Sierra western slope and mid-lake buoys (2)
- Some in 3 size modes; $PM_{2.5}$, PM_{10}, TSP in 2 week samplers; many 24 hr measurements in TSP alone
- Analysis for ~ 30 elements by DRI XRF
  - DRI - only 6 (out of 540) phosphorus values > MDL
  - No phosphorus values in attempted aircraft profiles
- Additional analyses – late in the project
  - UCD Geology 19 (out of 70) phosphorus values > MDL using ICP/MS
  - UCD DELTA Group 56 (out of 70) phosphorus values > MDL using S-XRF

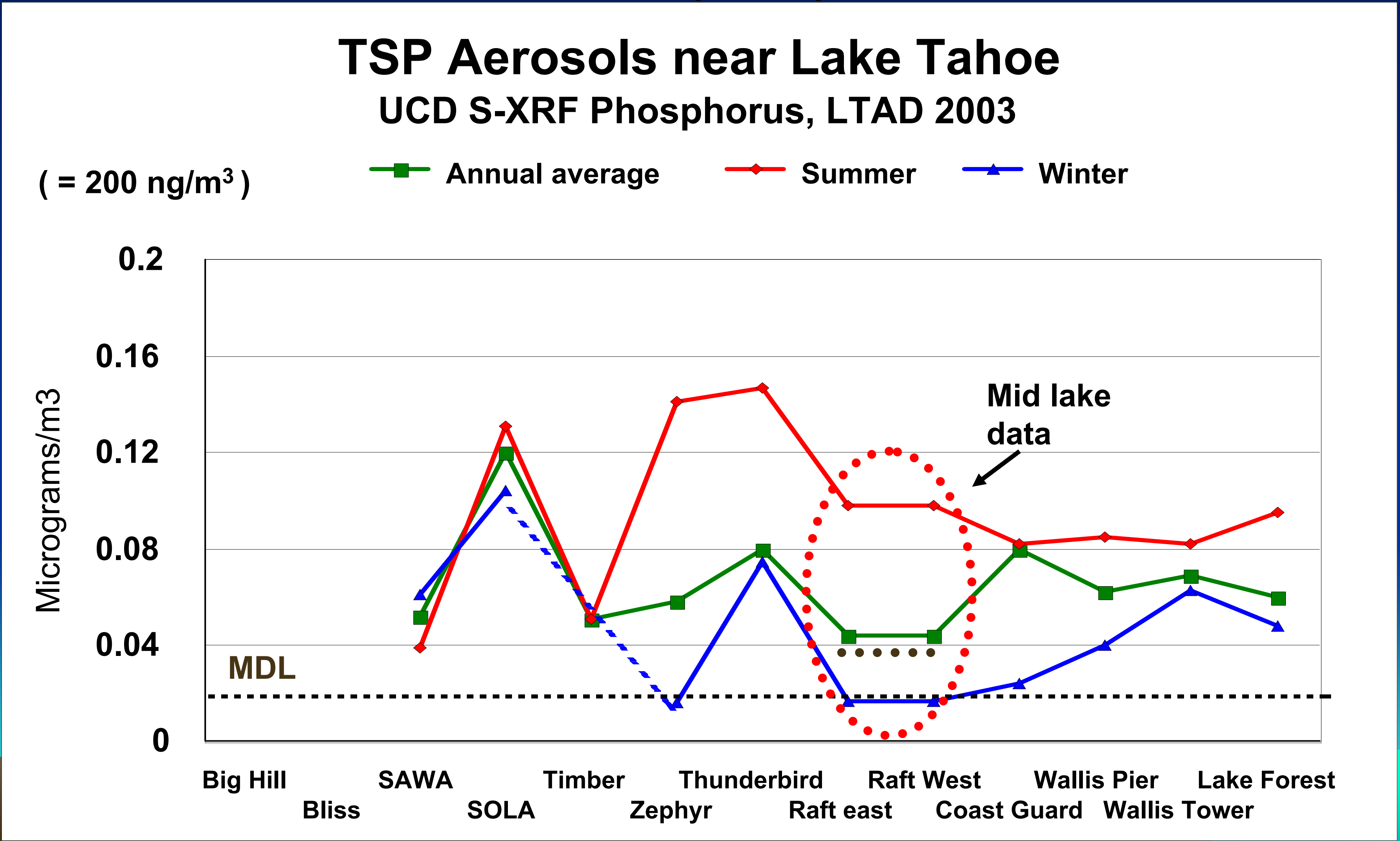
Approaches to enhance phosphorus values for LTAD

1) Accept 56 corrected phosphorus values, UCD/ S-XRF, by season and site; then interpolate
2) From existing phosphorus values, estimate MDLs
   a) not possible for DRI since only 6 out of 540
   b) Possible for UCD S-XRF , 56 out of 70 possible, but only 70 samples limit coverage
3) From 540 existing silicon values, estimate phosphorus
   a) Apply geochemical ratio for igneous rock, 0.5%
   b) Enhancement of phosphorus from dust seen in the UCD/TRPA work 2.78 ± 0.23 for particles > 2.5 μm

Estimation of phosphorus around Lake Tahoe from silicon data



Phosphorus results from 56 S-XRF analyses (14 missing values added at 0.5 MDL); note that these data include non-soil phosphorus like smoke



Other evidence on the precision and accuracy of the S-XRF phosphorus results

- All measurements made on the two rafts 8 km apart in summer on the same day were statistically identical,
  - June 23, 53 ng/m^3 west raft, 63 ng/m^3 raft (± 41 ng/m^3)
  - July 24, 143 ng/m^3 west raft, 133 ng/m^3 east raft (± 53 ng/m^3)
- The data often show a smooth progression along a transect Wallis/Coast Guard through the rafts to Thunderbird despite very different samplers, sampling times, and air volumes.
- The $PM_{2.5}$ phosphorus values at SOLA from LTAD filters, 28 ng/m^3, was very close to the $PM_{2.5}$ phosphorus from TRPA DRUMs, 2003, 24.5 ng/m^3.
- The average phosphorus values from ICP/MS were ~ 60% of S-XRF values in winter –spring (the only overlap periods) despite very different sample selection.

First order estimations of deposition

- Take measured annual phosphorus values, estimate v_d (Seinfeld and Pandis), multiply times lake area and time,
  - 3 to 11 tonnes/year due to the uncertainty in v_d over water.
- Take predicted phosphorus from soil via silicon, ~ 30 ng/m^3 with a 9 µm mode, get deposition velocity 0.8 cm/s and calculate deposition
  - 3.7 ± 1.3 tonnes/year soil alone
- Subtract soil phosphorus from total phosphorus to get non soil phosphorus , use lower v_d, and calculate deposition
  - 2.8 ± 2.0 tonnes/year, non soil
- Total dry deposition is the sum of the above
  - 6.5 ± 3.3 tonnes/year
- 2nd order deposition – match lake edge and center values, fall off, summer and winter, …..
-

Future analysis of phosphorus Lake Tahoe

- Urgent - Meet the needs of TRPA and Lahontan
  – Additional S-XRF analyses by Cliff and Perry of existing LTAD filters, at least 50 to 80, focusing on the rafts, the north end of the lake, and Big Hill.
- In process
  – UCD/CalTrans Highway 50 study, with an additional 10,000 phosphorus values in 8 size modes every 3 hr, winter and summer, at SOLA and Sandy Way ($93K, 4/5 completed, Final Report 6/30/2006)
  – Establishment of a south area Raft site with bucket deposition measurements. (TRG 2006)

Future analysis of phosphorus Lake Tahoe

- Mid Lake aerosol measurements on Rafts, north and south, by size, time, and full composition, including mass and phosphorus.
  - Fine particles are a major factor in lake clarity
- Continuous monitoring at key shore sites
  - Bliss SP, Tahoe City site, Thunderbird, Bijou, (Zephyr Cove?)
    - Routine analysis for mass
    - Selected analysis for phosphorus and fine particles
- Dedicated Quality Assurance site at Bijou, with TRG buckets (2), NDEP collectors, and redundant aerosol/analytical measurements including DRUM, IMPROVE (including PM_{10}), ARB BAMS, Minivol and Two Week Samplers.